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Determination of arsenic and mercury metals in suspended particulate matter by flame/flameless atomic absorption spectrometer

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ABSTRACT

A method has been developed for the accurate determination of arsenic and mercury deposited on suspended particulate matter (SPM) collected by high volume sampler (HVS) from various locations of Delhi (Capital city of India) by using hydride generator with flame/flameless Atomic Absorption spectrometry (AAS). Several diverse sites has been monitored for arsenic and mercury content in environment by analyzing the samples by the method proposed, but in the present study we are reporting data from seven diverse sites Ashram (S–1; heavy traffic zone), Azadpur (S–2; industrial zone), Loni Road (S–3; densely populated + traffic zone), Pitampura (S–4; urban background zone), Highway no. 56 (S–5; traffic zone), Naraina (S–6; industrial zone) and NPL (S–7; mix zone).

The standard deviation of the measurements has been calculated on the basis of six observations of two replicates (three each) of each analyzed species and was found to be less than 3.5% by the proposed method. The validity of the method proposed has been established by standard addition of arsenic and mercury in the procedureal blank (without sample) and also to check the loss during the process. It has been found that in five replicates, arsenic and mercury recoveries were 99.3±0.4% and 99.1±0.6% respectively within 95% confidence level. The method proposed is highly reproducible and can be used for accurate determination of arsenic and mercury in the atmospheric particulate matter samples. The arsenic concentration varied from 1.3±0.11 ng/m^3 to 5.1±0.27 ng/m^3, while concentration of mercury varied from 1.4±0.21 ng/m^3 to 12.5±0.81 ng/m^3, in seven diverse sites of the Delhi.

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1. Introduction

In the last few decades, environmental pollution due to toxic as well as heavy metals has been on the rise in some states of India due to open mining of different types of ores, industrial emissions (Khan et al., 2005; Kaushik et al., 2009) and road transport. World Health Organization (WHO, 2002) points out that outdoor air pollution contributes as much as 0.6 to 1.4% of the burden of disease in developing regions, and other types of pollution, such as lead in water, air, and soil, may contribute 0.9%. Several cations have their positive and negative effects on human beings and environment (Shevade and Ford, 2004). The various metals present in particulate matter play an important role as activator for the enzymatic–catalysis processes in human beings like Fe and Zn (Reilly, 1980; Holland et al., 1988) and they are essential for human health and serve as catalysts for fat oxidation. The effect of several other metals like Cu (Dell, 1976), Pb (Bellinger and Stiles, 1993) and Cd (Kaneta et al., 1986; Ducros, 1992) have been studied by various researchers on plants, animals and human beings. Besides these metals, mercury and arsenic have several negative effects on human health. The concentration level of arsenic and mercury in environmental samples may give information about the degree of pollution in the environment and will help us to determine the availability, mobility and chemical behavior (Dockery et al., 1993; Dockery et al., 1996) of such elements. The concentration of arsenic in $PM_{2.5}$ samples has been monitored at urban background monitoring station of the city of Huelva (Spain) during 2001 and 2002 (Sanchez de la Campa et al., 2008). Atmospheric aerosols have an important influence on regional climate and human beings globally. Each year, several thousands of cases of respiratory illnesses due to penetration of airborne particles into the human respiratory system (Milford et al., 1985) are associated with atmospheric pollution (Faiz and Sturm, 2000). Several sources of arsenic in PM_{10} have been discussed in rural site of Central Chile (Dell, 1976). Arsenic is present in four valence states (-3, 0, +3 and +5) in the environment. Under strong reducing conditions arsenic is found in (0), arsine (-3) valence state, under reducing conditions arsenite (+3) and under oxygenated environments as arsenate (+5). Inorganic arsenic is believed to be more toxic than organic arsenic and within these classes the trivalent form is more toxic than the pentavalent form. Fossil fuel burning, petroleum refining, mining, smelting of metals like Zn, Cu, Ni, and Pb, are the major anthropogenic sources for arsenic contamination in air, water and soil. Recent studies showed that lung cancer is significantly higher in the areas where arsenic concentration is 1.77 ng/m^3 or more (Navas-Acien et al., 2005; Yoshikawa et al., 2008). In last decades presences of arsenic and mercury in air/drinking water has become an issue of global concern (WHO, 2001; Joo and Cheng, 2006).

Fly ash also causes environmental pollution, which is another source of arsenic and mercury. Mercury is a potent neurotoxin found in a variety of products. It affects the brain, liver and kidneys

and can cause developmental disorders in children. Mercury and its organic compound methyl mercury is recognized as an environmental contaminant and known to be capable of damaging the central nervous system (USEPA, 1997; Davidson et al., 2004). The Environmental Protection Agency (EPA) sets a reference concentration of 0.3 μg/m^3 for inhalation exposure to mercury, while the National Institute for Occupational Safety and Health (NIOSH) set the exposure limit for mercury vapor as 50 μg/m^3. In literature there are several reported methods in which mercury has been determined in various matrices like the geochemical standard reference material (Ma et al., 2000; Ducker et al., 2005; Evans et al., 2001) in mining residue (Biester et al., 2000), and in rocks and sediments (Elrick and Horowitz, 1987). Arsenic have also been determined in urban road dust and in air at a traffic related site by Han et al. (2008) and Chiaradia and Cupelin (2000), respectively.

Therefore, it is of immense importance to determine the concentration levels of arsenic and mercury in the atmospheric samples, which directly influence the human health. Mercury and arsenic shows poor sensitivity when determined by conventional flame AAS. Another problem is related to digestion process in which most of the mercury and arsenic gets volatilized during chemical process. Therefore, it is important to convert volatile forms into nonvolatile forms during chemical process to avoid losses during wet digestion of the samples. In the present investigation an analytical method has been developed for the direct determination of arsenic and mercury in environmental samples by flame/flameless AAS respectively.

2. Experimental

2.1. Sampling site and description

New Delhi, the capital of India, is the second–largest metropolis in India, with over 17.3 million residents. Delhi is a land–locked state and is surrounded by Haryana in the west and Uttar Pradesh states in the east. The city is located in the central India, 160 km south of the Himalayas at latitude 28°24′N to 28°53′N and longitude 76°20′E to 77°20′E) with an altitude of 715 ft above the mean sea level (AMSL). The location of Delhi is on the western end of the Gangetic plain, which is drained by River Yamuna. New Delhi and its vicinity have a somewhat exaggerated continental climate due to its distance from the coast and location with respect to mountain ranges.

Delhi's climate is mainly influenced by its inland position and the prevalence of continental air during major part of the year. New Delhi is located in the subtropical belt with maximum temperature of 45 °C in summer and minimum temperature of 1 °C in winter. This area is under the influence of monsoonal winds (ranging from NE to NW in winter and ranging from SE to SW in the summer), with average yearly rainfall of approximately 73 cm. According to the Delhi Economic Survey (2008-09) report, in 2000–2001, Delhi registered 564 private vehicles (both cars and two-wheelers) a day. This jumped to 1 054 personal vehicles per day in 2006–2007 registering an almost two–fold increase. According to the report, Delhi's vehicular population had reached 5.6 million by 2007–2008, as against 3.0 million in 1997–1998, with an annual growth rate of 6.42%. Thermal power plants contribute to 13% and industrial activity contributes to 12% of air pollution as reported by the National Environmental Engineering Research Institute (NEERI, 1991), Nagpur. For the present study, seven different sites were selected namely Ashram (S–1) which is a heavy traffic zone and thousands of vehicles per hour crossing this junction, Azadpur (S–2) industrial zone which is also a densely populated residential area in North West Delhi District. India's largest wholesale market for vegetable and fruits–called the Azad Market–is the major land mark of Azadpur. Loni Road (S–3) is a densely populated area and also a traffic zone, Pitampura (S–4) is neither a heavy traffic zone nor a industrial zone, so we have considered this as an urban background zone, highway no. 56 (S–5) is a traffic zone, Naraina (S–6) is an industrial zone, and adjunct to Naraina to Mayapuri Industrial Area, NPL (S–7) is considered to be a mixed zone. Two sides of NPL is surrounded by ridge areas whereas other two sides are surrounded by residential areas, with traffic movement, at an about 1 km upwind of the sampling site. All the samples were collected between 9:00 am to 6:00 pm because of the major operational activities during daytime and since in the nighttime the filter papers get moist due to dew and flow rate of HVS also decreases sharply as a result of heavy loading of suspended particulate matter (SPM). The sampling was carried out between January 31 and February 7, 2008. The locations of sampling sites are marked in the map of Delhi, India, and presented in Figure 1.

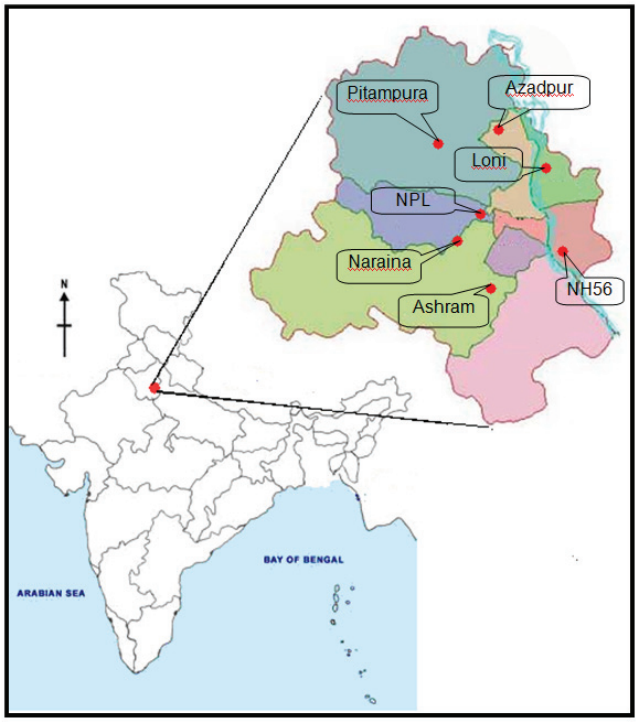

Figure 1. *Locations of sample collection in Delhi (capital city of India).*

2.2. Instruments and apparatus

The SPM sampling was carried out using a High Volume Sampler (HVS–410, Envirotech). SPM was collected on pre–desiccated cellulose filters using the high volume sampler. No chemical treatment of cellulose filter papers were carried out before sampling, but the filter papers were dried for 3 hours in an oven at 105 °C before sampling to remove the moisture if any and to get a constant weight. Flow rate of HVS was kept about 1.0±0.2 m^3/min. and the average sampling time was ~7.5 hours.

A Flame Atomic Absorption spectrometer (FAAS) (Analytik Jena, Vario–6) with a vapor generation accessory (AAS–HG) was used. Details of instrumental parameters are given in Table 1. The detection limits range between 1 μg/L to 1000 μg/L for FAAS, 0.05 μg/L to 100 μg/L for ICP–OES Emission–radial, 0.1 μg/L to 10 μg/L for ICP–OES Emission–axial, 0.005 μg/L to 0.1 μg/L for AAS–HG, 0.01 μg/L to 0.1 μg/L for GFAAS, and 0.001 μg/L to 0.01 μg/L for ICP–MS. Atomic absorption spectrometry is a superior technique in comparison to other techniques like, XRF and ICP–OES. Auto calibrateable transfer pipettes of 0.5–5 mL volume range from E. Merck (Germany) and volumetric flasks by Borosil glass works India Limited were used. All the acid digestion and dilution work was carried out in a cleaned laminar flow bench equipped with a proper ventilation system.

Table 1. *Details of FAAS Instrumental and set parameters for the analyzed elements*

Equipment: Analytik Jena Vario–6 Absorption Spectrophotometer (Flame) (wave length range:190–900 nm)				
Element	**Lamp Made by**	**Wavelength (nm)**	**Slit width (nm)**	**Flame conditions (L/min)**
Arsenic	Analytik Jena	193.7	0.2	Electro–thermal heating up to 900 °C
Mercury	Analytik Jena	253.7	0.2	Room temperature

2.3. Reagents

Nitric acid (69%) and hydrochloric acid (35%) of GR grade (Guaranteed Reagent) were purified by Sub–boiling distillation using quartz glass device, Potassium iodide, sodium hydroxide, ascorbic acid, hydrogen peroxide (35%) and sodium borohydride (99%). As and Hg present in trace amounts in the acid were further removed by distillation. After distillation, these sub–boiled Nitric acid and hydrochloric acid were used as reagent for As and Hg determination to avoid background contamination of As and Hg. Millipore Milli–Q de–ionized water (18.2 mega ohm resistivity) was used throughout the process.

2.4. Instrument calibrations

The calibrations of the AAS for arsenic and mercury were carried out with certified reference standard solutions covering the desired concentration range of the analyte in the sample. The reference standards stock solution of 1 000 mg/L of arsenic and mercury were procured from SCP Science of USA. The stock solutions of SCP Science (1 000 mg/L) were further diluted in the range of 5 µg/L to 50 µg/L for calibration of AAS for arsenic and mercury. The diluted standard solutions of arsenic and mercury used for calibration of AAS were further compared with certified reference standard solution prepared by National Physical Laboratory, India (NPLI).

3. Procedure

Two replicates of 9.25 × 11.75 cm size (known weight at deposited area) of all the seven sites were taken for the determination of arsenic and mercury into cleaned PTFE vessels separately. The cleaning of PTFE vessels were carried out by socking them in 5% nitric acid for 24 hours before analysis and further washing them several times with Millipore Milli–Q de–ionized water (18 MΩ). Further, 15 ml of sub boiled nitric acid, 5 mL of hydrogen peroxide, and 5 mL of DI water were added to these vessels and they were closed with airtight lids. The PTFE vessels–containing samples were kept for overnight at room temperature. Then, the PTFE beakers were digested on hot plate after adding 4 to 5 drops of sulfuric acid at temperature range 160 °C–180 °C by covering them with a lid of Teflon for at least 2 hours until the solution got to a thicker condition. Again the samples with residue were heated on the hot plate with 10 mL of concentrated hydrochloric acid, after thicker condition, the samples were heated once again with 5 mL hydrochloric acid to ensure a complete removal of nitric acid. Finally, the solutions were boiled with 15 mL 1:1 water hydrochloric acid mixture. After digestion the whole content was centrifuged at 5 000 round per minutes for three minutes to separate solid particles from the solutions. The whole precipitates were washed several times with hot water to ensure complete transfer of digested sample from the vessel. The final volume was adjusted to 50 mL by deionized water.

Further the known volumes of the stock solutions were heated at 75 °C for 45 minutes with 10 mL of 25% potassium iodide and 15 mL of 25% ascorbic acid solution to convert As (V) to As (III). The final solutions were adjusted to 50 mL by deionized water. In the solution, arsenic was determined by hydride generator after reducing in presence of sodium borohydride (3%), sodium hydroxide (1.5%) and hydrochloric acid (1%) using electro–thermal heating at 900°C, while mercury was determined in the stock solution using the same condition at room temperature using respective standards and principal resonance line of each element. Mean absorbance values of three readings of two replicates (three each) were taken into consideration for calculation of each analyte element. Procedural blanks for cellulose filter paper without sample were also run to check the blank levels for both elements and blank correction applied wherever required. The standard addition (of known quantity–100 µg/kg, 5 mL of 1 000 µg/kg in 50 mL volumetric flask) procedure was also applied for arsenic and mercury in the beginning and processed same as the samples to check the losses during the preparation process and to check the reliability of the wet digestion.

4. Results and Discussion

A new approach for sample dissolution was adopted for the volatile analytes like arsenic and mercury in the suspended particulate matter collected from air at different sites. In an earlier method, the SPM sample is digested directly in 5% nitric acid. After filtration, the final sample solution was always found turbid because the fine particles passed through the filter paper, and this turbidity causes error during analysis. It is also difficult to filter out metallic species with several washings and traces of metals remaining on the filter paper during filtration while in centrifuge, the solid particles get easily separated compared to simple filtration. However, 100% transfer is not possible, there is always loss of metals during filtration and they may remain with the precipitate but here the recovery is better than the simple filtration.

It is also important that final arsenic solution should not be in an oxidizing medium during analysis, so it is important to convert it into a reducing state otherwise it will not be possible to convert arsenic to arsenic hydride (AsH_3) by reaction with solution of sodium borohydride, sodium hydroxide and hydrochloric acid.

In the proposed method, dissolution in nitric acid and hydrogen peroxide in closed Teflon vessels reduces the losses during digestion due to conversion of arsenic and mercury into oxidizing states. After completion of digestion process, the solution was centrifuged to separate solid and as well suspended particles from the solution. Thus the final solutions obtained by the proposed method were clear and no turbidity appeared even they were kept for long periods. The proposed method gives reproducible results for arsenic and mercury in the samples within 95% confidence level. Table 2 shows the details about the standard parameters for collection of sample through HVS, while Figure 2 shows the variation of SPM collected from various sites of Delhi. Table 2 shows that ambient air concentration of SPM in Loni Road was 2 337 µg/m^3, which is almost 5.5 to 11.5 times higher compared to the remaining sites. All samples have been analyzed in duplicate and three measurements of each replicates were carried out. The results are given in Table 2, which covers an average of the three measurements of two independent weighing of each sample.

The arsenic concentration was found to range from 1.3±0.11 to 5.1±0.27 ng/m^3. The variation in concentration of the arsenic and mercury at various sites of Delhi depends upon the transport, industrial and other anthropogenic activities. The maximum concentration of arsenic was found at Ashram zone (S–1 site; 5.1±0.27 ng/m^3) and minimum concentration was found at Pitampura and NPL zone (S–4, S–7; 1.3±0.11 ng/m^3). The high concentrations of arsenic at Ashram are mainly due to transport, industry and thermal power plant in the area. In Loni Road area which is a densely populated zone, the household activities, industrial emissions and transportation contribute to the relatively

high arsenic contamination in the air. The arsenic concentration varies from one country to another probably due to industrial and traffic emissions. In a study carried out in Spain during 2001–2002 on $PM_{2.5}$, an average As concentration of 6.4 ng/m^3 has been reported (Sanchez de la Campa et al., 2008) which is higher than the one observed at Ashram zone (S–1). According to the study by Yoshikawa et al. (2008), lung cancer is significantly higher in the areas where arsenic concentration is 1.77 ng/m^3 or higher. Therefore from Table 3 it is evident that five sites out of seven sites monitored in the present study had higher arsenic concentrations than the prescribed limit. Thus, these are the highly risky zones due to high level of arsenic content in the air.

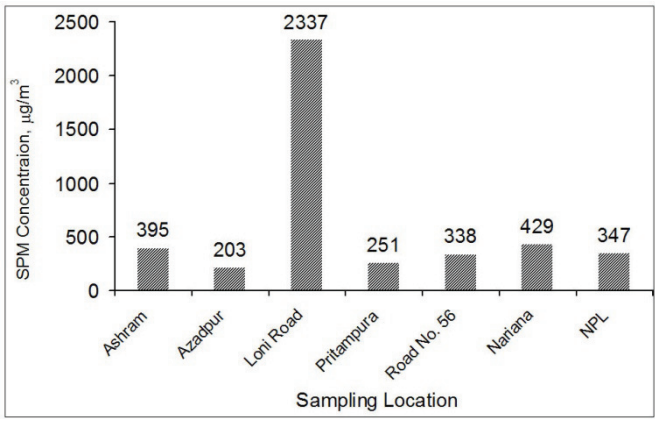

Figure 2. *Variation of SPM concentration between January 31 and February 7, 2008.*

Similarly, concentration of mercury varies from 1.4±0.21 ng/m^3 to 12.5±0.81 ng/m^3 in all the seven sites (Table 3). The lowest concentrations of mercury were found at Pitampura site (S–4; 1.4±0.21 ng/m^3), while in Loni Road it was the highest (S–3; 12.5±0.81 ng/m^3). The high concentrations of mercury at Ashram (S–1; 10.8±0.52 ng/m^3), Loni Road (S–3; 12.5±0.81 ng/m^3), Azadpur (S–2; 5.1±0.46 ng/m^3) and Narina (S–6; 5.0±0.36 ng/m^3) thought to have resulted from anthropogenic influences. As elemental mercury is used in a variety of household products, including thermostats, glass thermometers, barometers, and switches in large appliances. Fluorescent bulbs also contain mercury vapor and a larger amount of mercury in a powder or dust form is emitted into the air if the bulb breaks. So, these are the probable sources of mercury in this zone.

The uncertainty of measurements has been reported as the standard deviations of three readings of duplicate samples. The blank level of arsenic and mercury in two cellulose filter paper (in 10 × 10 cm area sample used for digestion and volume adjusted to 25 mL), were found to be 5.2±0.3, 7.1±0.3 mg/L respectively, while in quartz filter paper the concentration of arsenic and mercury were found to be 14.2±0.3 mg/L, 10.8±0.4 mg/L respectively. This concentration includes acids and other background from sample digestion. The detection limit for arsenic is 0.001 µg/mL and for mercury 0.0005 µg/mL using hydride generator. All the data reported have been corrected for the blank value.

In chemical methodology it is a common problem, that matrix matched reference standards are not available. Other reference materials like NIST reference material Fly ash 1 633(b) cannot be compared to atmospheric SPM due to matrix differences. A quantitative estimation was conducted for fly ash using lithium tetraborate fusion and 1 633(b) reference material was used for

Table 2. *Volume of air processed through high volume sampler (V_{HVS}) at STP*

Name of the site	Date of Sampling	Sampling starting time	Sampling end time	Flow rate of air sampled through HVS (m^3/min)[a]	Time (min)	Volume of air processed through HVS (m^3)	Atmospheric pressure measured on site (mbar)	Atmospheric Pressure in mm of mercury (mbar×0.75)	Average temperature of the site (°C)[a]	Volume of air processed through HVS at STP at 25°C (m^3)
Heavy traffic zone (S-1): Ashram	31-1-08	9.10 am	5.30 pm	1.0 ± 0.2	500	550	994.2 ± 0.55	745.65	24 ± 3	541.4
Industrial zone (S-2) : Azadpur	1-2-08	10.0 am	5.00 pm	1.0 ± 0.2	420	462	995.2 ± 0.55	746.40	24 ± 3	455.3
Densely populated + traffic zone (S-3): Loni Road	2-2-08	9.45 am	5.30 pm	1.0 ± 0.2	465	511.5	993.6 ± 0.55	745.20	25 ± 3	501.5
Urban background zone (S-4) : Pitampura	3-2-08	9.45 am	5.30pm	1.0 ± 0.2	465	511.5	992.5 ± 0.55	744.37	25 ± 3	500.9
Traffic zone (S-5): Highway No.56	4-2-08	10.30 am	6.30 pm	1.0 ± 0.2	480	528	995.5 ± 0.55	746.63	26 ± 3	516.9
Industrial zone (S-6): Nariana	5-2-08	9.15 am	6.00 pm	1.0 ± 0.2	425	467.5	996.3 ± 0.55	747.22	26 ± 3	458.1
Mix zone (S-7): NPL	6-2-08	10.0 am	4.40 pm	1.0 ± 0.2	400	440	992.8 ± 0.55	744.60	26 ± 3	429.6

[a] For the calculation of air processed through HVS the flow rate of HVS was taken as 1.1 m^3/minute, while the temperature was taken as 24°C in case of S-1, S-2 and 25°C in case of S-3.

Table 3. *Results of arsenic and mercury in SPM analyzed by flame/flameless AAS*

Name of the site	SPM in µg/m^3	Concentration of Arsenic in (ng/m^3)	Concentration of mercury in (ng/m^3)
Heavy traffic zone (S-1): Ashram	395	5.1 ± 0.27	10.8 ± 0.52
Industrial zone (S-2) : Azadpur	203	2.9 ± 0.18	5.1 ± 0.46
Densely populated + Traffic zone (S-3): Loni Road	2 337	3.9 ± 0.21	12.5 ± 0.81
Urban background zone (S-4): Pitampura	251	1.3 ± 0.11	1.4 ± 0.21
Traffic zone (S-5): Highway No.56	338	1.6 ± 0.12	2.7 ± 0.15
Industrial zone (S-6): Nariana	429	2.1 ± 0.13	5.0 ± 0.36
Mix zone (S-7): NPL	347	1.3 ± 0.11	3.9 ± 0.25

± Standard deviation of six measurements (three each) of two replicates

traceability (Singh et al., 2003). The fly ash is a complex matrix and arsenic and mercury cannot be released without adding HF and upon adding HF, the majority of arsenic and mercury get lost during digestion. However, SPM is not complex matrix and As and Hg are absorbed on the surface of SPM, which can be released easily without adding HF. Considering these facts, the results were further verified by standard addition in which known quantity of mercury and arsenic solutions were added at the beginning of the process and the sample was processed as above and it has been found that in five replicates of arsenic and mercury recovery were 99.3±0.4% and 99.1±0.6% respectively within 95% confidence level. KI has serious interference in the determination of mercury, for precaution the tubes of hydride generator could be washed several times to avoid interference and all the glassware also preheated before using. It will be better to analyze mercury first, then arsenic to avoid the interference of potassium iodide.

5. Conclusion

To determine the concentration of toxic trace metals like As and Hg is of high interest, mainly for human beings. Therefore, it is very necessary to have a rapid and accurate method of determination of these elements in environmental samples. Flame Atomic Absorption Spectrometry has been found to be a rapid, reliable method for the analysis of arsenic and mercury. In the present investigation, a specific analytical method has been developed for the evaluation of volatile species present in SPM sample like As and Hg by Flame and flameless AAS using hydride generator. The vapor generation technique/cold vapor technique with AAS provides an accurate and sensitive determination of As and Hg in atmospheric particulate matter samples collected through a high volume air sampler. By using the proposed method, it is possible to determine As and Hg with good precision and accuracy. In this study we are reporting the data of seven sites collected in first week of February 2008. We are making efforts to collect and analyze the SPM samples seasonally, so that one can mitigate the probable sources of these contaminants and precautionary action could be taken before they are emitted into the atmosphere.

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